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REPORT

WITCO Corporation

Laboratory Treatability Study Report

Oxidation of Carbon Disulfide in Soils — Halby Chemical Site, New Castle, Delaware

2 July 1996

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1.0 OVERVIEW

1.1 BACKGROUND

The former Halby Chemical, New Castle, Delaware (Halby) site was used for the production of primarily thiocyanate-based or related products for approximately 50 years. Occasional discharges of wastewaters or other materials containing carbon disulfide (CS_2) over a number of years resulted in deposition of CS_2 in site soils. Soils containing elevated CS_2 levels have been identified to exist in a former ditch area between the plant and an on-site lagoon. Levels of CS_2 in soils in the ditch area range up to 110,000 mg/kg, with an average concentration of approximately 10,000 mg/kg CS_2. The affected soils comprise up to 11,000 cu. yd., depending on the delineation concentration. The soils are generally below the water table and are, therefore, saturated.

1.2 TREATABILITY STUDY RATIONALE

From February to June, 1995, EPA conducted preliminary work that indicated that a combination of air oxidation and hydrogen peroxide could be used in an aboveground treatment process to oxidize CS_2 in the soils.

In June 1995, various remedial contractors were interviewed by Langan Engineering and Environmental Services, Inc. (Langan) to propose means of full-scale treatment of affected soils. The vast majority of contractors proposed excavation, chemical treatment of the soils, with or without dewatering, containerization, and transport to an off-site landfill. The remaining contractors proposed biological treatment, vapor-phase removal of carbon disulfide (with vapor treatment), or vitrification.

Concurrently, Witco Corporation (Witco) commenced a parallel investigation of feasible treatment methods by researching treatment methods, reviewing the previous EPA work, contacting CS_2 manufacturers, and obtaining records of decision (RODs) from other CS_2-contaminated sites.

Discussions between Langan and two carbon disulfide manufacturers (ICI and Akzo Nobel) indicated no treatment processes that had been employed on the quantity of soil and the concentration of carbon disulfide found in the Halby soils. Soil slurrying, with subsequent boil-off of CS_2 was deemed suited only for smaller quantities of soil. Air stripping (with or without emissions controls) was proposed; however, the saturated condition of the soils might reduce the effectiveness of this alternative. Because of the elevated CS_2 concentrations in the Halby soils, this process would also likely require CS_2 vapor controls that would increase the complexity of the remedial system. Mineral oil extraction of CS_2 and subsequent incineration was proposed; however, this would be costly on a large scale. Sodium hypochlorite oxidation was believed to have the potential for undesirable byproduct formation. Hydrogen peroxide oxidation at low concentrations (3 to 5 percent) and at pH 10 was suggested and was deemed a promising means of CS_2 removal in preference to air stripping with off-gas treatment.

Literature reviews were conducted (including, but not limited to, Chemical Abstracts, American Chemical Society databases, EPA and other governmental databases) to determine additional sources of information on CS_2 oxidation of soils or aqueous streams. Appendix A, which represents a fraction of the CS_2 references reviewed, presents those references deemed applicable to treatability of the Halby CS_2 soils. In general, the review found little information pertinent to soil treatment for CS_2. The most promising reference found was that of Adewuyi, U.G. and G.R. Carmichael, 1987, "Kinetics of Hydrolysis and Oxidation of Carbon Disulfide by Hydrogen Peroxide in Alkaline Medium and Application to Carbonyl Sulfide," (Envir. Sci. & Tech. 21: 170-177). This article described the stoichiometry and reaction mechanism for the oxidation, indicating that the presence of the hydroxyl radical and hydrogen peroxide is key, and provided valuable background information that formed a partial basis for the treatability work performed in the bench-scale studies.

Site investigation work by both EPA (July 1995) and Witco (December 1995) indicated that the CS_2-containing soils were both combustible and potentially explosive when exposed to air. Moreover, CS_2 and sulfide odors were observed upon excavation of the soils. As a consequence, it was decided that in situ treatment would be more effective to mitigate these difficulties and that chemical oxidation was the most desirable option for in-situ treatment.

1.3 *TREATABILITY STUDY GOALS*

The purpose of the bench-scale treatability studies conducted on CS_2 oxidation in soils was to investigate and develop an effective, in-situ treatment for the oxidation of CS_2 present in soils at the Halby Chemical site. Specifically, the aim of the studies was to gather information on the following treatment process factors:

- relative oxidation reagent performance,

- appropriate reagent dosage, pH, reaction time, and reaction temperature,
- efficiency of CS_2 removal under the various reaction conditions,
- off-gas constituents,
- effects on other constituents in the soil, and
- experimental observations that pertain to full-scale implementation of the technology evaluated.

1.4 *RAW SOIL DESIGN BASIS*

Two soil types were used for the bench-scale treatability studies summarized in this report: a non-Halby soil believed to contain no CS_2, which was used for initial spiked-sample experiments (see Section 2), and the Halby soil containing CS_2 that was used for the bulk of the experimental work.

The non-Halby soil used for spiked sample evaluations was a silt-sand mixture obtained from the Rio Grande river bed in Albuquerque, New Mexico. This soil source was used because of its proximity to the treatability laboratory. A qualitative evaluation of the non-Halby soils was made by mixing an aliquot of the soils with 50% hydrogen peroxide. The purpose of this test was to determine whether peroxide-reactive materials were present in the soils. No apparent reaction was observed, indicating that the non-Halby soils did not have any readily oxidizable material that would interfere with the experiments.

The Halby soils were obtained from the area of the former on-site drainage ditch at depths known to contain elevated levels of CS_2. Two 5-gallon soil samples were obtained from the site on 2 and 3 April 1996 according to the plan submitted to the EPA by Langan on 25 March 1996. Samples were collected for analysis at the site to determine the initial concentration of CS_2 present. The two soil samples were then immediately shipped under chain-of-custody to the ECD laboratory in Albuquerque, NM, where they were stored under refrigeration until needed. Three analyses were performed on the two samples obtained from the site, with the following CS_2 levels: 54,000; 31,000; and 17,000 mg/kg, respectively (averaging 34,000 mg/kg).

After receipt at the laboratory, one of the five-gallon samples was homogenized and further subdivided into five one-gallon samples and each one-gallon subsample analyzed. The analysis results for those samples were: 27,000; 53,000; 17,000; 54,000; and 22,000 ppm respectively. Because of the variability in concentration, an average of 34,000 mg/kg (the average of both sets of results) was used to represent the baseline CS_2 concentration used to calculate reagent additions for treatability study design.

2.0 TREATABILITY TEST PROCEDURES

2.1 TREATABILITY TEST OVERVIEW

The oxidation of CS_2 in alkaline solution studied by Adewuyi and Carmichael (1987) follows the equation

$$CS_2 + 8H_2O_2 + OH^- \rightarrow HCO_3^- + 2HSO_4^- + 2H^+ + 6H_2O$$

The oxidation process produces bisulfate ions, which are acidic, and act to retard further reaction of CS_2 with the peroxide as the pH decreases. In order to counteract the decrease in pH, reactions must be carried out under alkaline conditions. The purpose of the testing was to determine the factors that drove this reaction to completion in the Halby soils.

Four sets of bench-scale experiments have been completed, as follows:

- studies using spiked non-Halby soils,
- small-scale studies using Halby soils,
- large-scale studies using Halby soils, and
- focused studies using Halby soils for quantification of process parameters.

The first study (conducted in early to mid-April 1996) was designed to determine overall oxidation characteristics for various oxidants on the non-Halby soil spiked with CS_2. The second study (conducted in mid- to late April 1996) determined whether the reaction between oxidants and CS_2 occurred in Halby soils and the extent to which it occurred with different oxidants. The third study (May 1996) provided verification of the results of the initial studies, with an evaluation of the significance of pH levels, moisture content, and time of the reaction. The fourth study (late June 1996) was designed to answer questions related to off-gas composition, hydrogen peroxide-caustic oxidation dynamics, and the fate of non-CS_2 organics. The results of these experiments are reported in Section 3.

2.2 REAGENTS AND EQUIPMENT

2.2.1 Treatability Reagents

Chemical additives were used for two purposes in the experimental program: as oxidizing agents, and as pH adjustment/maintenance compounds.

Three oxidizing chemicals containing hydrogen peroxide were employed in the testing: hydrogen peroxide in aqueous solution, sodium percarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$), and sodium perborate ($NaBO_2 \cdot H_2O_2 \cdot 3H_2O$). Sodium persulfate ($Na_2S_2O_8$) does not contain hydrogen peroxide, but is a powerful oxidant and so was selected for comparative trials. Other peroxide carriers and oxidizers were considered (sodium peroxide, ozone, oxygen) but they were not evaluated in the studies, since they offered few advantages or several disadvantages relative to the four oxidants considered herein.

Hydrogen peroxide (50%), sodium percarbonate, sodium perborate, and sodium persulfate were obtained from Aldrich Chemical Company under product numbers 42,065-4; 37,143-2; 24,412-0; and 21,623-2, respectively. Sodium carbonate and sodium bicarbonate (both buffering compounds) were obtained from the same supplier as product numbers 22,353-0 and 23,652-7, respectively. Sodium hydroxide was also used for pH control in certain trials using hydrogen peroxide.

The buffer solution prepared from the sodium carbonate and sodium bicarbonate consisted of one gram of sodium carbonate and one gram of sodium bicarbonate per 20 milliliters of water.

2.2.2 Treatability Test Equipment

Spiked sample and small-scale testing (as defined in Section 2.4.1) was conducted in 500- and 1,000-ml pyrex round-bottom flasks (either one-necked or three-necked, with 24/40 ground glass joints). Large-scale tests, including supplemental tests, (as defined in Section 2.4.1) were carried out in two-liter reaction kettles with temperature control jacketing. The kettles consist of a base and a top that is clamped and sealed with a teflon o-ring. The top is a three-neck 24/40-joint type. Figure 1 shows a typical reaction vessel set-up for the small- and large-scale experiments.

The gas capture experiment employed a three-neck, 1,000-ml round-bottom flask, with 24/40 joints. Off-gas was captured in 500-ml gas capture bulbs with stopcocks at each end of the bulb. The off-gas exiting the bulb was directed into a water bath to ensure positive displacement of gas in the bulb as the reaction proceeded. Figure 2 shows the reaction vessel and off-gas collection equipment for this experiment.

Samples were stirred within the flasks and kettles using a stainless steel folding vane mixer for small samples and the gas collection sample, and a prop mixer for large samples. A teflon vacuum adapter was used for the stirring mechanism to provide a gas tight seal.

Materials of construction for the materials employed in the testing were pyrex, stainless steel, and teflon.

Temperature and pH measurements were made with both an electronic pH meter/temperature probe and a glass thermometer.

2.3 *SAMPLING AND ANALYTICAL SCOPE*

The samples were stored under refrigeration (at 0°C) prior to use. Excess sample (i.e., that not used in the experiments) will be returned to the site for treatment during the field implementation phase of the program. An inventory of sample use was kept to account for all sample used in the experiments. Treated samples aliquots not held for analysis and excess soils were stored in sealed steel containers at room temperature.

Initial small-scale samples, as described further in this document, were analyzed during the treatability studies using screening methods for short-turnaround analysis. Large-scale samples were analyzed using standard procedures, including (as appropriate) EPA CLP methods and quality assurance/quality control procedures to ensure that the data gathered in the study were reliable.

The measurement of pH was carried out for screening purposes during the treatability studies using a Hanna Instrument pH meter/temperature probe calibrated at pH 4. 7, and 10 using Fisher standard solutions. Additional laboratory pH measurements were conducted on large-scale samples.

2.3.1 *Raw Soil Sample Analysis*

Raw soil samples were taken at the time of collection of soils for the treatability effort from the site. After receipt at the treatability laboratory, additional confirmatory samples were taken. Both sets of samples were analyzed for CS_2 according to CLP SOW OLM03.0 with revisions. Laboratory data packages for these analyses are presented in Appendix B.

2.3.2 *Spiked Soil Sample Analysis*

Spiked soil samples were analyzed for CS_2 and pH. The CS_2 analysis was conducted using a high-performance liquid chromatography (HPLC) procedure, as presented in Appendix C. A calibration curve was prepared for the instrument from 5,000 mg/kg to 625 mg/kg CS_2, which is also provided in Appendix C. Several experiments were made to check the extraction and quantitation procedure (mini method validation). In addition, lower-concentration samples at levels as low as 60 mg/kg were run to check the linear accuracy of the standard curve, which was found to be acceptable for screening purposes. After calibration of the HPLC, four samples (100 grams each) were spiked with CS_2 from 1% to 2% by weight (10,000 to 20,000 mg/kg) and allowed to equilibrate for 24 hours in the soil at room temperature by the procedure described in Section 2.4.2. They were then extracted with methanol for at least 24 hours and analyzed via the HPLC. Spike recoveries of 70 to 85% were obtained. These results indicated that the HPLC method was acceptable for screening use. Continuing calibration samples run with the matrix spikes indicated that the HPLC maintained its standard response to CS_2.

2.3.3 *Small-Scale Sample Analysis*

Small-scale samples (as defined in Section 2.4.1) were analyzed for the same parameters using the same methods as those for the spiked samples.

2.3.4 *Large-Scale Sample Analysis*

Large-scale samples (as defined in Section 2.4.1) were analyzed by Envirotech Research and its subcontractor, Galbraith Laboratories, using EPA-approved and other standard procedures, with CLP deliverables for target compound list and target analyte list analyses. All or some of the following analytes, depending on the sample nature, were analyzed: CS_2 (CLP SOW OLM03.0 with revisions), chemical oxygen demand (COD) (sample leaching using ASTM D3987-85, followed by analysis by EPA Method 410.4), pH (SW-846 Method 9045), elemental sulfur (ASTM D4239), total and leachable metals (arsenic, manganese, beryllium, and copper) (SW-846 Method 6010 and SW-846 Method 1311 (TCLP)), and thiocyanate (sample leaching using ASTM D3987-85, followed by analysis by ASTM D4193-89). Volatile compounds plus tentatively identified compounds (TICs) (SW-846 Methods 8260) were analyzed in one sample submitted separately to Hall Environmental Laboratory (Hall Environmental) in Albuquerque, New Mexico. All samples were shipped under chain of custody on ice in a sealed container to maintain sample integrity. Available supplemental analytical information for these samples is provided in Appendix B to this report.

2.3.5 *Supplemental Large-Scale Sample Analysis*

Analytical work for the trials performed under the supplemental phase of the treatability studies consisted of CS_2, COD, thiocyanate, elemental sulfur, and pH, performed according to the methods used for the large-scale sample analysis. Volatile and semivolatile analyses conducted on one sample for byproducts determination were conducted by Envirotech Laboratories using CLP (SOW 3/90) procedures. Available supplemental analytical information for these samples is provided in Appendix B to this report.

2.3.6 *Off-Gas Testing*

Off-gas was collected from one sample in the supplemental large-scale round of testing to determine the presence of selected constituents. The analysis of the sample was performed by Hall Environmental. Carbon disulfide and carbonyl sulfide, as well as other volatile organics, were analyzed using SW-846 Method 8260. Results from this analysis are pending.

2.4 *EXPERIMENTAL CONDITIONS*

2.4.1 *Overview*

The experiments performed on both spiked non-Halby and Halby soils used the same reagents and generally similar reaction conditions and requirements. The sample to be treated must contain adequate water to allow mixing of the reagents and yet retain soil consistency. The maximum quantity of water required to be added as buffer or by dilution of 50% hydrogen peroxide was determined through observations made during the course of the experiments.

The site soils employed in the treatability testing were maintained in such a manner as to preserve their original characteristics. This included maintaining sealed containers, with limited pre-experiment homogenization so as to obtain representative results. Reactions were carried out in a buffered or alkaline-pH medium (in this case very moist soil, with added buffering solution when needed). The buffer or caustic concentration supplied adequate basicity to maintain the reaction rate. In cases where sodium percarbonate or sodium perborate (inherently buffering compounds) were used as the oxidant source, buffer volume was decreased in order to conserve chemicals and not cause an excessively high pH condition in site soils.

Using the average concentration of CS_2 values in the one-gallon subsamples of untreated soil, a theoretical oxidant requirement was calculated. The stoichiometric requirement of oxidant as a percentage of the soil sample to be treated was derived from the above equation as the concentration of CS_2 in percent times 3.578[1]. This value was then adjusted for the presence of a carrier such as water (e.g., 50% hydrogen peroxide solution is 50% water) or other inert material.

Spiked soil studies were conducted on 50- to 100-gram soil samples. Small-scale studies on Halby soils were conducted on 100-gram soil samples; large-scale and supplemental studies were conducted on 500-gram samples, except for the gas generation study sample, which was a 200-gram sample.

Reaction conditions were allowed to vary, depending on the objective of the experiments. For those experiments designed to determine conversion of CS_2, the reaction was carried out at atmospheric pressure and room temperature (25°C). For those experiments designed to evaluate the heat of reaction, the experiments were started at temperatures as low as 0°C and allowed to reach an equilibrium temperature (no more than 80°C)[2].

Spiked soil and small-scale studies were carried out using a reagent addition/oxidation time of 30 minutes. Reactions were stopped at 30 minutes by adding dilute hydrochloric acid, and analyses were performed within 15 minutes after reaction termination. Large-scale studies were conducted using a reagent addition/oxidation time of 8 hours to avoid excessive sample overheating.

2.4.2 *Spiked Soil Testing*

Initial screening of the reaction between the oxidants and CS_2 was done on the non-Halby soils spiked with CS_2. Fifty-to-100-gram samples of non-Halby soil were containerized and spiked with CS_2 at a target concentration of 1,000 mg/kg. The soils were sealed, parafilmed, and allowed to equilibrate for 24 hours at approximately 21°C, with little or no headspace.

1. The calculation is expressed as weight of oxidant required equals the molecular weight of hydrogen peroxide times eight divided by the molecular weight of carbon disulfide.

2. Although this temperature is above the boiling point for CS_2 (46°C) and well above the flash point (-30°C), it is still below the autoignition temperature (100°C). There were no signs that the reaction mix had combusted spontaneously.

Experiments were then run on these soils using caustic for pH adjustment and 50% hydrogen peroxide as the oxidant (see Table 1). For the first series of tests, the caustic (1 equivalent of sodium hydroxide) and peroxide (8 molar equivalents) were added to the soil simultaneously (these were the stoichiometric quantities necessary for theoretical 100% reaction of the CS_2). In a second experiment, 24 molar equivalents of peroxide (three times theoretical) and the same quantity of caustic (1 equivalent) were used. A control experiment using only caustic (no oxidant) was run concurrently with those where peroxide was added, and an overall control with no oxidant addition or pH adjustment was also run.

Additional spiked soil experiments were carried out with the solid oxidants (percarbonate and perborate) at 8:1 molar ratios of oxidant to the spiked non-Halby soils. The experiments used the bicarbonate/carbonate buffer instead of caustic to neutralize the acid generated by the oxidation reaction.

2.4.3 *Small-Scale Soil Testing*

The purpose of the small-scale experiments was to examine the extent of the oxidant reaction with the CS_2 and to evaluate heat released. Initial experiments to measure reaction temperature rise were conducted at room temperature using the solid oxidants. Following these experiments, two additional experiments were conducted under controlled temperature conditions to see whether there was a significant impact of volatilization of the CS_2 when the reaction temperature was observed to reach the 60-80°C level. The addition rates are shown in Table 2. Necessary oxidant doses, preferential oxidation of CS_2 versus other organics, and required reaction time were examined. Vapor generation was evaluated qualitatively. Further, two experiments (H-4 and H-5) were carried out to determine whether there was a relationship between the quantity of oxidant added and the residual CS_2. These tests were carried out at a level of 10% of the theoretical dose of oxidant, with the results compared to those at stoichiometric dosages of oxidant.

The batch experiments were carried out on small-scale (100-gram) samples of Halby site soils using the oxidants hydrogen peroxide, sodium percarbonate, sodium perborate, and sodium persulfate. The approximate average CS_2 concentration of untreated soils (34,000 mg/kg) was used to calculate the addition of oxidant to soil in experiments in this series. The theoretical quantities of reactants (expressed as the complete oxidant formula) are summarized in Table 3 (assuming that the average concentration of CS_2 in the Halby soils is 34,000 mg/kg and an 8:1 ratio of oxidant to CS_2 is theoretically correct).

Twenty milliliters of the bicarbonate/carbonate buffer were added to the 100 gram soil samples treated with percarbonate and perborate. In the case of peroxide, 10 ml of 0.1 N sodium hydroxide was added. The reactions were carried out in 200 ml sample jars with hand agitation. The temperature of the reaction mix was measured with a glass thermometer inserted into the reaction mix.

2.4.4 *Large-Scale Soil Testing*

Large-scale studies were carried out to provide adequate sample size to allow analysis by a certified laboratory using EPA-approved procedures. The purpose of these analyses was to verify the screening-procedure results obtained earlier in the experimental program. A secondary objective of the experiments was to evaluate reaction effectiveness (conversion of CS_2 by the various oxidants) so that field treatment could be fine-tuned to the existing concentrations. One additional test run was made to clarify the potential for byproduct formation during the oxidation process.

The format of the experiments was as follows: 500 grams of Halby site soil were placed in a 2-liter resin kettle. An aliquot of the same soil was sampled at the time the resin kettle was charged in order to establish an initial (untreated) concentration of CS_2. Experiments were carried out with each of the oxidants successfully screened so far: sodium percarbonate, sodium perborate, and hydrogen peroxide. (Sodium persulfate was not found to be a successful oxidant.) The percarbonate and perborate were added directly as solids to the Halby soils. The hydrogen peroxide was added as a 25% solution to minimize local overheating of the reaction mix. One hundred ml of buffer solution composed of 50 ml each of 0.1 N sodium carbonate and sodium bicarbonate were added to the reaction mix prior to the addition of percarbonate or perborate. One hundred ml of carbonate/bicarbonate buffer were used for the hydrogen peroxide trial: fifty ml of carbonate (0.1 N) were added to the Halby soils prior to the addition of hydrogen peroxide, and fifty ml of bicarbonate buffer solution (0.1 N) were subsequently added to make a 25% peroxide solution (from 50% stock). The individual experiments with the oxidants were carried out at the molar ratios provided in Table 4 of oxidant to CS_2 (assuming an initial CS_2 concentration of 34,000 ppm).

Note that the stoichiometric ratio of oxidant to CS_2 which is needed to oxidize all CS_2 is 8 moles of oxidant (as equivalent hydrogen peroxide) to each mole of CS_2. The experiment using an 8:1 molar ratio of hydrogen peroxide was not considered practical as a soil treatment method for soil quantities with this high of an average CS_2 content. This is because of the significant heat generation of the reaction. Eight-hour addition times were used to moderate temperature rise; however, the temperature rise was still significant. Subsequent experiments (Section 2.4.5) further investigated ways to mitigate the temperature rise of the reaction. A lower molar ratio (4:1) was used rather than additional dilution, which would cause the reaction mix to become a thin slurry.

The tabulated molar ratios indicated above were based on initial CS_2 concentrations of 34,000 mg/kg. In practice, laboratory analysis of each sample tested indicated significantly lower initial levels of CS_2. The results presented on Figure 3 reflect the actual molar ratios of oxidants added to the levels of CS_2 based on CLP method analysis.

The reaction mass was continuously cooled and agitated throughout the addition of oxidant. Cooling was achieved through the use of an external ice bath. The temperature of the kettle could be lowered by submerging the bottom of the kettle to remove the heat generated by the reaction. The reaction mass was kept below 25°C throughout the experiments to minimize the loss of CS_2 through volatilization. Temperature was monitored continuously by hand. Agitation of the reaction mix was carried out by manually stirring the reaction mix.

Reaction conditions were similar to those for the small-scale trials, except that the oxidant was added over an 8-hour period to avoid a high heat generation rate. Although previous small-scale studies indicated that no external buffer solution was required for the percarbonate solid oxidant, aqueous buffer solutions were employed in these large-scale trials to aid in heat dissipation and to maintain consistent reaction conditions among oxidants. Because of potential safety and cost concerns with caustic use for pH adjustment in the hydrogen peroxide trials, the 0.1 N carbonate/bicarbonate buffer used with solid oxidants was employed.

In a special experiment, 200 grams of Halby soil were treated at an 8:1 molar ratio with hydrogen peroxide and the soil submitted for volatile organic analysis, as described above. An untreated soil sample was also sent for analysis at the same time this experiment was started. The purpose of analyzing these samples was to evaluate the presence of non-priority list (non-target) chemicals in the samples (such as carbonyl sulfide).

2.4.5 *Supplemental Large-Scale Testing*

To verify selected results of previous treatability work, additional focused tests were conducted as follows, for the reasons given:

- hydrogen peroxide/caustic trial at a target oxidant to CS_2 ratio of 2:1, an oxidant addition time of approximately five hours and a total reaction time of 24 hours, with a reaction temperature of less than 45°C. A slow rate of oxidant addition was used in lieu of sample cooling to depress the overall reaction temperature. The caustic was added at a 1:1 ratio relative to the CS_2.

This trial sought to evaluate the improved oxidation performance afforded by caustic instead of buffer addition and to complete the lower end of the dosage-percent removal curve for hydrogen peroxide.

- hydrogen peroxide/caustic trial at a target oxidant to CS_2 ratio of 4:1, an oxidant addition of approximately five hours and a total reaction time of 24 hours, with a reaction temperature of less than 45°C. A slow rate of oxidant addition instead of sample cooling was used to depress the overall reaction temperature. The caustic was added at a 1:1 ratio relative to the CS_2.

  This trial was designed to evaluate the improved oxidation performance afforded by caustic instead of buffer addition and to complete the intermediate portion of the dosage-percent removal curve for hydrogen peroxide.

- sequential caustic addition over a 72-hour period, followed by hydrogen peroxide addition over a 5-hour period within an overall reaction time of 24 hours. Caustic was added at a 1:1 ratio to relative to the CS_2. The hydrogen peroxide was added at a 4: 1 molar ratio of oxidant to CS_2. An initial reaction temperature of 8°C was provided. No ice bath was used for this experiment; only air cooling was used. The final reaction temperature was between 45 and 50°C.

  This trial was performed to determine the effect that the sequential addition of reagents has on reducing the significant heat generation achieved from the concurrent reaction of caustic and hydrogen peroxide.

- hydrogen peroxide/caustic trial at an oxidant to CS_2 ratio of 4:1. The caustic was added at a 1:1 ratio relative to the CS_2. Temperature was controlled by slow addition of the oxidant to the soil. The oxidant addition/reaction period was approximately three hours, over which two 500-ml bulbs of off-gas were collected. The bulbs were vented (after the sample collection point) through a water bath to ensure positive displacement of the off-gas and, hence, a representative sample of the reactor off-gas.

  The purpose of this test was to generate off-gas from the reaction in sufficient quantity to enable analysis for reaction byproducts.

In the 2:1 and 4:1 peroxide/caustic trial, as well as the 4:1 gas generation experiment, 2.2 g or 4.4 g, respectively, of caustic were dissolved in 10 ml of water and mixed with the peroxide prior to adding the mixture to the soil.

3.0 TREATABILITY TEST RESULTS

3.1 PHYSICAL REACTION AND TREATED SOIL CHARACTERISTICS

3.1.1 Reacted Soil Consistency

The reaction between the oxidants and either CS_2 or other oxidizable materials in the soil was apparent upon observation of the reaction mass. The reaction produced effervescence within the soil as the oxidant was added. The solid reagents reacted readily with contaminants; however, mixing of the solids was not uniform, and the reaction mass was not homogeneous in temperature. Since the solid oxidant powders were added at the top of the soil mass, it was hotter (as much as 10°C higher) there than at the bottom of the mass. The reaction mass resembled "mousse" in consistency after addition of the solid reagents. Hydrogen peroxide addition resulted in a more fluid consistency to the soil than that observed for the solid oxidants.

3.1.2 Reaction Temperature

Figures 3 and 4 indicate the temperature increase observed in the small-scale samples with solid oxidant (perborate and percarbonate) addition over time. The graphs indicate that the equilibrium temperature of the mixtures was in the 60-80°C range. This temperature is the result of heat generation in the reaction mix and cooling of the uninsulated reaction vessel by the air in the laboratory. It appears that, in this equilibrium temperature range, the heat generation is equal to the heat loss from the uninsulated sides of the reaction vessel. As indicated by the temperature increase measured in the first few minutes of the reaction, the heat release is about 20 kcal/g-mole of solid oxidant. As the reaction proceeded, the increment of temperature increase per quantity of oxidant added decreased substantially.

In subsequent small-scale studies in which cooling of the reaction mix was conducted, the initial temperature for the percarbonate addition was 0°C. After percarbonate addition, the temperature increased to 34°C, where it was maintained until all of the reagent was added. At these lower temperatures, the percarbonate appeared to react readily, although the reaction was much less vigorous, with lesser heat generation than from peroxide and a lower equilibrium temperature in the reaction mass. The perborate reaction was much slower, and the reaction temperature did not increase to above 5°C over the 30-minute oxidant addition period. It was not until the sample was allowed to warm to room temperature (approximately 17°C) after the 30-minute oxidant addition period, that the sample with sodium perborate started to react.

3.2 *CONSTITUENT REMOVAL EFFICIENCIES*

3.2.1 *Carbon Disulfide Removal*

Results of the evaluation of different oxidants on CS_2-spiked soils are summarized in Table 1. As may be seen from the initial results, all of the tested oxidants except sodium persulfate were able to achieve substantial CS_2 removal. Sodium persulfate was tested under small-scale sample conditions at an 8:1 molar ratio of oxidant to CS_2; however no reaction or reduction of CS_2 was observed.

Caustic alone was able to achieve removal of CS_2 equivalent to those with peroxide oxidants. However, as noted below, the reaction end products are bisulfide and sulfide, which are undesirable. Spiked soils treated with caustic and peroxide yielded nondetectable residual CS_2 levels (extrapolated below the lowest HPLC standard calibration point of 625 mg/kg).

The results of the small-scale experiments using solid oxidants (percarbonate and perborate) are provided in Table 2. Carbon disulfide reductions observed in small-scale samples treated with 1/10 of the stoichiometric dosage of peroxide and percarbonate were approximately an order of magnitude lower than those achieved at stoichiometric oxidant addition levels. This supports the proportional relationship between oxidant level and residual CS_2.

Large-scale results for CS_2 oxidation are presented in Table 5 and summarized in Figure 5. The actual untreated CS_2 concentrations were used in calculating the percent reductions in CS_2 presented on Table 5 and Figure 5, rather than the previously assumed level of 34,000 ppm CS_2. The calculations adjusting for the actual CS_2 concentrations in the soils being tested are provided in Table 6.

The data from the large-scale trials (including supplemental trials) shown in Figure 5 indicate that 90+ % conversion (equal to residual CS_2 concentrations in the range of 400 mg/kg, based on raw soil levels) can be reached by percarbonate or perborate oxidation at a molar ratio of oxidant to CS_2 of 8:1 to 11:1. This is at or near the projected stoichiometric ratio of 8 moles of oxidant to one mole of CS_2. Levels of 200 mg/kg or lower can be obtained at molar ratios of 15 to 17:1. The large-scale trials using hydrogen peroxide as the oxidant, but with buffer instead of caustic, were not as successful as those for other oxidants tested, likely because of the low resultant oxidation pH. A subsequent test (H-25) was performed using hydrogen peroxide, with caustic at a 1:1 molar equivalent of CS_2 to caustic. This test achieved a CS_2 reduction equivalent to that obtained in other higher-oxidant-dose oxidation trials, yet at a pH below the literature-based threshold value of 8.5.

3.2.2 *Chemical Oxygen Demand Removal*

Chemical oxygen demand (COD) was run on all large-scale samples (Table 5) to assess the degree to which organics other than CS_2 were being degraded during the oxidation. In general, modest to no change in COD occurred. However, in certain samples (tests H-6, H-12, H-16, and H-18), the COD after treatment increased by approximately 16,000 mg/kg. This would indicate that COD-refractory compounds in the soil were being oxidized to COD-amenable compounds.

For the hydrogen peroxide trials (tests H-19 and H-23), the low pH may have caused preferential oxidation of organics other than CS_2. The two remaining elevated COD samples were run using much less than stoichiometric quantities of oxidant. This should not have resulted in an increased degree of organics oxidation to COD-amenable materials, unless a threshold quantity of oxidant is required for CS_2 oxidation, below which other COD will be oxidized preferentially. It is noted that all the trials run at stoichiometric or higher oxidant ratios exhibited nominal change in COD, and only one trial below stoichiometric levels of oxidant addition showed a nominal change in COD.

3.2.3 *Removal of Other Constituents*

Thiocyanate analyses were conducted on tests H-22 through H-25 and H-25A from the supplemental large-scale testing. Results are presented in Table 7. The results for tests H-22 through H-25 indicated that between 8 and 24 percent of thiocyanate was removed in oxidation with hydrogen peroxide in the presence of caustic. Raw soil levels of thiocyanate were 13,700 and 8,010 mg/kg, with treated soil levels of 10,400 and 7,360 mg/kg, respectively. The thiocyanate removal observed in the sequential addition of caustic and hydrogen peroxide (H-25A) is significantly higher. Whether this result is related to the changed reagent addition regime in this test cannot be concluded based on one sample; future work will attempt to clarify this issue.

Results of elemental sulfur analyses are provided in Table 7. The increased levels of this element in treated versus untreated soils indicate that the complete conversion (to sulfate) is being halted at an intermediate step, in which elemental sulfur is being generated. Of four pairs of samples analyzed, the two pairs exhibiting 75 percent or lower CS_2

removal showed increasing elemental sulfur levels in the treated samples. The two sample pairs displaying greater than 85 percent CS_2 removal showed decreasing elemental sulfur levels in the treated samples. While theoretically an acidic pH results in increased conversion to elemental sulfur, whereas an alkaline pH causes conversion to sulfate, the sample set analyzed was not sufficiently large to conclusively show this trend.

3.3 *REACTION BYPRODUCTS*

Although initial results using caustic alone indicated comparable removal efficiencies for CS_2 relative to other oxidants, there are byproduct issues associated with this reaction that should be noted. The reaction of caustic (without other oxidants) with CS_2 in the soil would not reach completion (conversion of the CS_2 to sulfate) and would be very slow in the absence of a pH of at least 10.5. As a result, caustic addition alone would leave the soil with large bisulfide and sulfide concentrations, or a high pH, neither of which is appropriate for full-scale remediation.

One concern associated with pH adjustment of the soils was that presently nonleachable metals might become leachable. To address this issue, total and leachable arsenic, beryllium, copper, and manganese were analyzed. The results are presented in Table 8. Note that the TCLP results are preliminary, representing filtered samples that have not yet undergone final digestion. Final results will be forthcoming shortly. These results indicate that the metals are not of concern from a leachability standpoint. The effect of treatment is evident on the solubility of arsenic, with solubility decreasing significantly after treatment. Beryllium was not detected in the leachates. Copper and manganese solubility appeared to increase following treatment. The copper levels observed may be a function of pH, which (for the treated samples) was not in the range of minimum solubility for this metal. Manganese data generally reflected the tendency of lower solubility with increasing pH.

Two tests have been run to assess the presence of volatile or semivolatile analytes or tentatively identified compounds (TICs) other than CS_2 that would represent byproducts in the treated samples. In the first trial, performed as part of the large-scale testing, no other compounds were detectable because of the elevated CS_2 levels in the sample. The second test was on a supplemental large-scale test H-25. Volatiles results from this sample indicated no other standard analytes, and only two TICs were observed: a $C_8H_{18}O$ alcohol apparently unrelated to the CS_2 oxidation and an unknown. Semivolatile results are presently being generated.

Gaseous reaction byproducts can also be generated by the reaction zone conditions, particularly when elevated reaction temperatures are allowed to persist. In the uncooled small-scale reactions, some volatiles appeared to be emitted from the reaction mixture, particularly in the first five minutes of the reaction. These were believed to include CS_2 and ammonia. Experiments to quantify and identify the nature of volatile emissions were recently conducted; however, results of emissions testing are not yet complete. In small-scale trials in which the reaction mix was cooled and maintained at or below approximately 35°C, there were few or no apparent CS_2 vapors observed to be emitted from the reaction.

3.4 *OTHER CONSIDERATIONS FOR FULL-SCALE TREATMENT*

The spiked soil sample treated with the 24:1 molar ratio of peroxide to CS_2 reacted violently and with generation of significant heat. The small-scale experiment employing 50% hydrogen peroxide at an 8:1 molar ratio of peroxide to CS_2 was also characterized by an excessively vigorous exothermic reaction, such that no data could be taken on the sample. These results suggest that lower ratios of peroxide added in a gradual manner are needed for practical full-scale application to contaminated soils. In addition to modifications to the rate of oxidant addition to reduce temperature, soil cooling via air, water, or other means may need to be considered to ensure appropriate soil temperatures are maintained.

In the small-scale comparison of hydrogen peroxide and percarbonate oxidation without buffering for pH control, it was found that both reactions proceeded in the absence of buffer addition, although the hydrogen peroxide reaction was less efficient than the percarbonate oxidation under these conditions. Consequently, it appears that a stronger base than the buffer (e.g. caustic) is needed to maintain hydrogen peroxide reaction efficiency.

4.0 CONCLUSIONS AND RECOMMENDATIONS

4.1 OXIDANTS AND REACTION CONDITIONS

The results obtained in the treatability studies indicate that hydrogen peroxide, perborate, and percarbonate were effective in oxidizing CS_2 in the Halby soils; persulfate was unreactive and showed no oxidizing ability. The conversion of CS_2 is dependent on the quantity of oxidant used, expressed as the molar ratio of oxidant to CS_2, and varies based on the oxidant used. This relationship is shown in Figure 5. Using the relationships identified in Figure 5, the quantity of the desired oxidant can be estimated to achieve a target residual concentration of CS_2.

The reaction variable having the most apparent impact on oxidation efficiency (other than oxidant dosage) is pH, which should be kept at 8.5 or higher for best results.

When oxidant and buffer (or caustic) were added simultaneously to large-scale samples, eight-hour oxidant addition/reaction times were required for 500-g samples of soil (versus 0.5-hour times for 50-100-g samples) to avoid significant heat generation. This indicates that heat generation rates increase faster than the increase in sample volume, a factor that will need to be considered in full-scale process logistics and economics. Process logistics will need to consider the width and depth of soil that can be treated at one time without generating such heat that significant off-gasing of CS2 and other constituents occurs. Process economics will need to reflect the increased time for remediation required to avoid undue heat generation. A promising means of mitigating the heat generation of the reaction may be indicated by the results of the sequential caustic soak/hydrogen peroxide addition, which significantly reduced the heat generated by the reaction. Additional testing is presently being conducted to better define the effect of the two-part addition of reagents.

Sodium perborate is not desirable for use because borate is a byproduct, and the perborate also causes significant soil temperature rise (50 °C), and is excessively costly. Perborate does have some inherent buffering capacity, and it maintains the soils treated in a semisolid form. Sodium percarbonate is acceptable for use based on its oxidation properties, lack of toxic byproducts in the treated soil, high inherent buffering capacity, moderate soil temperature rise (40 °C), and resultant soil consistency; however, its cost is high relative to that of hydrogen peroxide. Hydrogen peroxide has the lowest cost and generates no toxic byproducts in the treated soil; however, caustic appears to be needed to maintain a sufficiently high pH for the reaction to proceed efficiently.

The reaction between hydrogen peroxide and CS_2 at concentrations of CS_2 greater than about 1,000 ppm generates significant heat (through oxidation of both sulfur and carbon). Observations made during these treatability studies indicate that hydrogen peroxide cannot be handled at greater than a 4:1 molar ratio of oxidant to CS_2 without significant heat generation. At greater dilutions of the peroxide, the soil becomes excessively fluid.

4.2 *REACTION BYPRODUCTS*

Gaseous byproducts arising from the reaction are presently being determined. Control of reaction temperature is important to limiting volatilization of constituents from the soils. Significant heat was generated with all three successful oxidants, at levels estimated at 20 kcal of excess heat/mole of CS_2 oxidized for perborate and percarbonate.

Volatile reaction byproducts in the soils were not observed, based on the results of one analysis of a sample treated with hydrogen peroxide and caustic (Sample H-25). Semivolatile compounds are presently undergoing analysis to check for byproducts.

4.3 *RECOMMENDATIONS FOR FIELD TESTING*

The purpose of the field-scale testing will be to identify site-related constraints that could adversely affect successful implementation of in situ CS_2 treatment and to develop sufficient data to enable more definitive cost estimation for the selected process.

Based on the results of the bench-scale studies described herein, the following recommendations are made for inclusion in the field test design:

- testing of up to four treatment regimes for the affected soils:
  - one-step addition of caustic dissolved in hydrogen peroxide (up to two trials),
  - sequential addition of caustic and hydrogen peroxide,
  - addition of percarbonate and buffer solution,
- maintenance of reaction pH at or above 8.5, and
- provision of off-gas containment and controls to prevent potential off-site or worker impacts from treatment.

Because the bench-scale testing done to date can only approximate field conditions, these recommendations will be expanded upon in the field, depending on conditions encountered.

4.4 *FULL-SCALE TREATMENT COSTS*

Based on an assumed volume of 11,000 cu. yd. of soil requiring remediation, at an average concentration of 10,000 mg/kg CS_2, chemical costs for sodium percarbonate at the dosages to reach nondetectable levels would total $2.5 million. Corresponding chemical costs for hydrogen peroxide would total $800,000. For comparison, perborate costs would total $3.6 million. These costs will be reevaluated once cleanup targets are established with EPA.

Additional remedial costs consist of mobilization of equipment, implementation of the desired treatment scheme in full scale, controlling off-gases from the process, demobilization of equipment, and final grading of the site area affected. These costs will be better defined once contractors have submitted bids for completion of the full-scale work, following completion of field treatability studies.

Figure 1
Small- and Large- Scale
Oxidation Apparatus

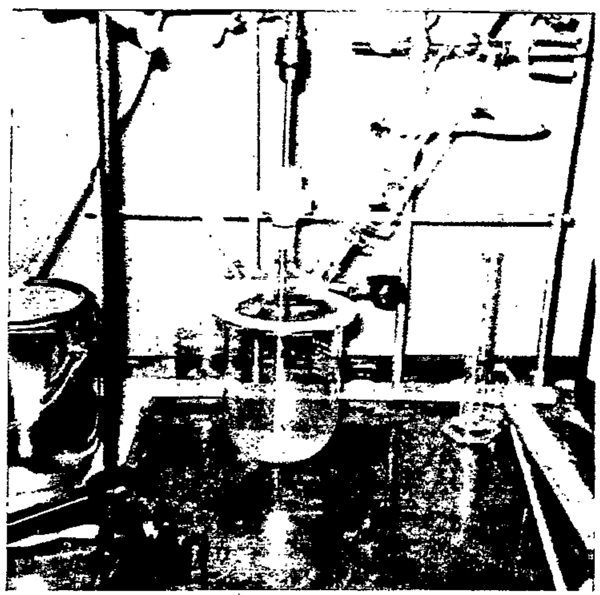

Figure 2
Gas Extraction Experiment Apparatus

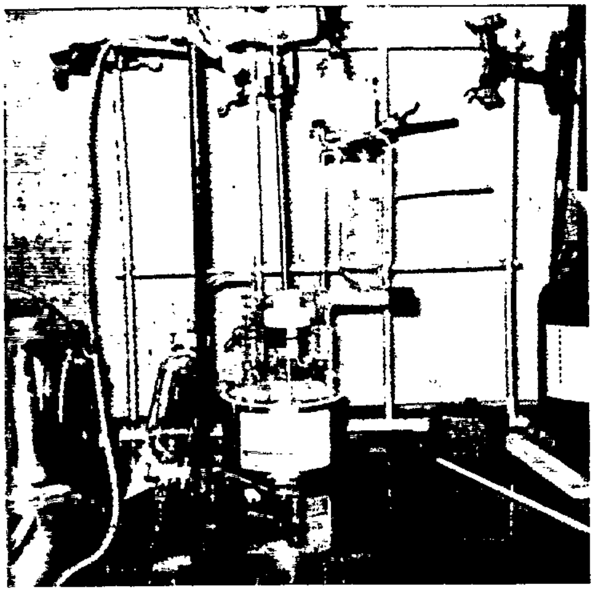

Figure 3
Reaction Mix Temperature Increase with Sodium Percarbonate Addition

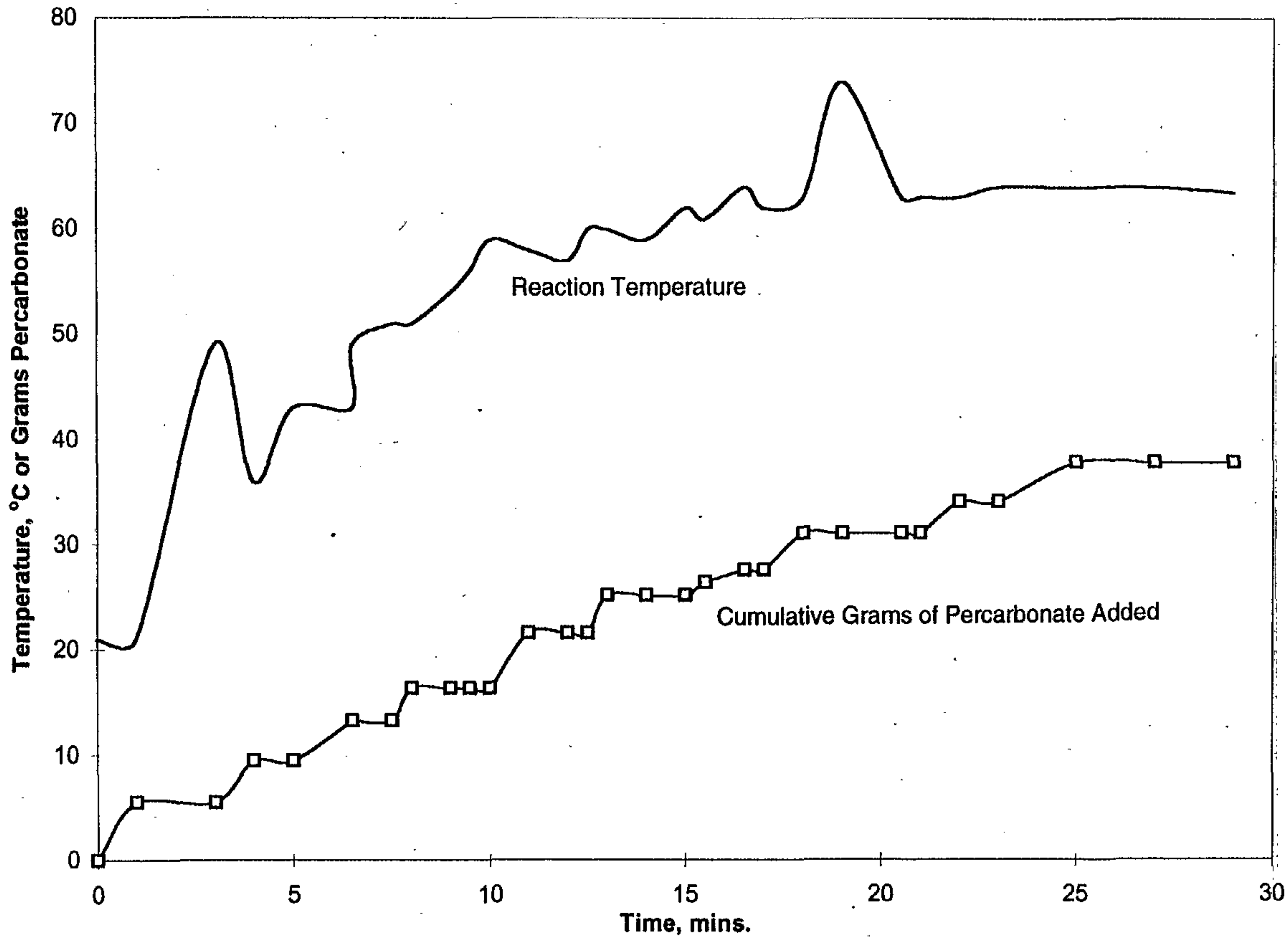

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Figure 4
Reaction Mix Temperature Increase with Sodium Perborate Addition

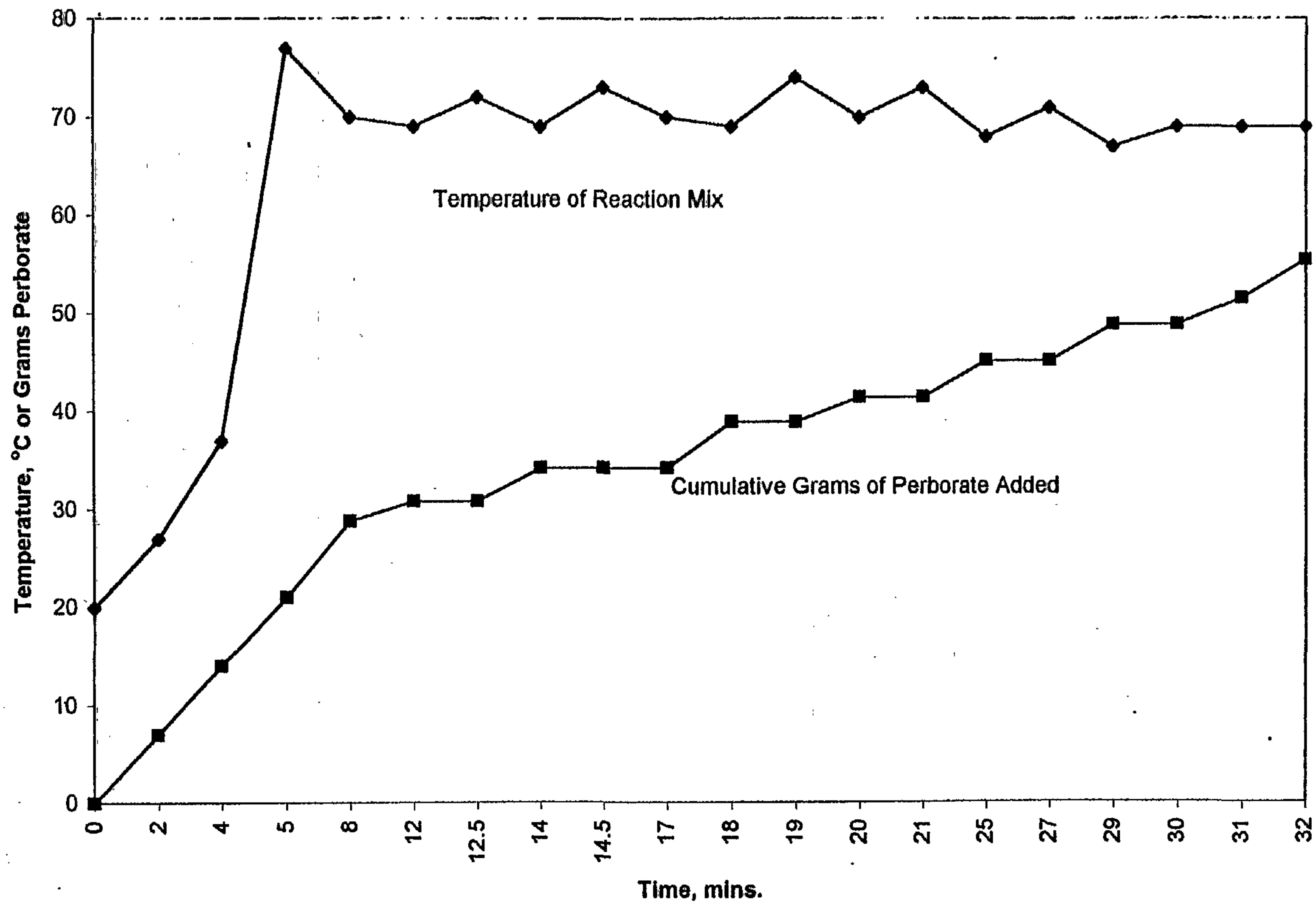

Figure 5
Conversion of Carbon Disulfide Versus Mole Ratio of Oxidant to Carbon Disulfide

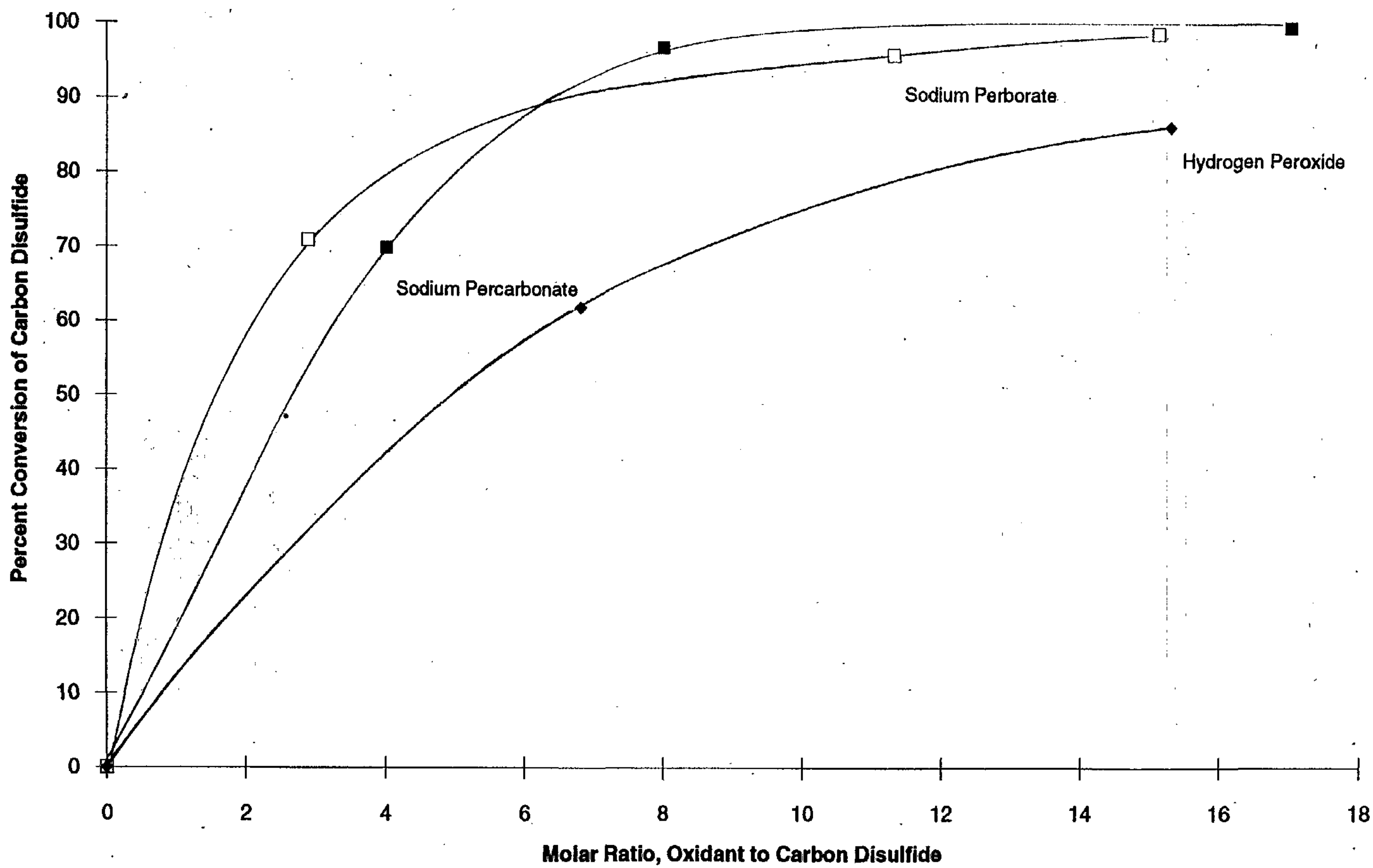

Table 1 *Non-Halby Spiked Soils Reacted at Varying Oxidant: CS_2 Molar Ratios*

Sample Size (g)	Initial Carbon Disulfide Conc. (mg/kg)	Oxidant	Caustic and/or Buffer	pH**	Unreacted Carbon Disulfide, mg/kg	Percent Reduction
50	1,000	None	NaOH	8.7	150	85
50	1,000	H_2O_2 (8:1)	NaOH	9.5	*	>99
50	1,000	H_2O_2 (24:1)	NaOH	9.8	*	>99
100	1,000	None	50/50 Carb.-Bicarb.	7.6	503	49.7
100	1,000	H_2O_2 (8:1)	50/50 Carb.-Bicarb.	8.4	157	84.3
100	1,000	Perborate (8:1)	50/50 Carb.-Bicarb.	9.1	144	85.6
100	1,000	Percarbonate (8:1)	50/50 Carb.-Bicarb.	9.6	213	78.7
100	1,000	None	None	—	918	8.2

All experiments carried out at room temperature
Soil samples allowed to react for 24 hours prior to analysis
* assumed negligible, based on substantial observed volatilization of CS_2 from the sample and vigorous reaction upon addition of peroxide. No CS_2 peaks were observed in the analysis of the treated samples.
** pH values recorded during oxidant addition for screening purposes only.

Table 2 *Small-Scale Halby Soil Samples Reacted Under Controlled Temperature (≤ 25°C) Conditions*

Sample ID	Buffer	pH**	Oxidant	Ratio Oxidant:CS_2	%CS_2 Reduction
Untreated	Carb/Bicarb	—	none	NA	5%
H-2	Carb/Bicarb	—	Percarbonate	8:1	not measured*
H-3	Carb/Bicarb	—	Perborate	8:1	not measured*
H-4	Carb/Bicarb	9.3	Percarbonate	0.8:1	approx. 10%
H-5	Carb/Bicarb	9.1	Perborate	0.8:1	approx. 11%
H-6	Carb/Bicarb	9.9	Percarbonate	8:1	99.9%
H-7	Carb/Bicarb	9.5	Perborate	8:1	80%

*These experiments were made to check temperature rise and heat generation. They are not considered reliable for calculating CS_2 reductions.

** pH values recorded during oxidant addition for screening purposes only.

Table 3 *Small-Scale Halby Site Soils Experimental Matrix*

Grams Halby Soil	Buffer Volume, Type	Grams Percarbonate	Grams Peroxide	Grams Perborate	Grams Persulfate
100	20 ml 50/50 0.1N Carb:Bicarb	38.7			
100	20 ml 50/50 0.1N Carb:Bicarb			56.9	
100	10 ml 0.1N NaOH		25.4		
100	20 ml 50/50 0.1N Carb:Bicarb				9.38

Table 4 Large-Scale Halby Soil Study Molar Ratios

Hydrogen Peroxide	Sodium Percarbonate	Sodium Perborate
2:1	2:1	2:1
4:1	4:1	4:1
—	8:1	8:1

Table 5 *Performance Data from Treatment of Halby Site Soils*

Sample ID	Sample Make-up	Oxidant/CS_2 Molar Ratio	CS_2 (ppm)	pH	COD (ppm)	%CS_2 Reduction
H-6	Untreated Halby Soil/Buffer (carb/bicarb) Solution	None	17,000	9.02	33,400	—
H-7	Treated Halby Soil/Buffer Solution/Percarbonate	4.0	5,000	10.03	46,500	70
H-8	Untreated Halby Soil/Buffer Solution	None	17,000	8.90	34,500	—
H-9	Treated Halby Soil/Buffer Solution/Percarbonate	8.0	440	10.06	30,500	97
H-10	Untreated Halby Soil/Buffer Solution	None	16,000	8.86	24,600	—
H-11	Treated Halby Soil/Buffer Solution/Percarbonate	17.0	4.1	10.26	25,000	99.9
H-12	Untreated Halby Soil/Buffer Solution	None	23,000	9.10	38,000	—
H-13	Treated Halby Soil/Buffer Solution/Perborate	2.9	6,600	9.96	54,100	71
H-14	Untreated Halby Soil/Buffer Solution	None	12,000	9.32	33,200	—
H-15	Treated Halby Soil/Buffer Solution/Perborate	11.3	400	10.32	28,200	96
H-16	Untreated Halby Soil/Buffer Solution	None	10,000	9.58	27,600	—
H-17	Treated Halby Soil/Buffer Solution/H_2O_2 (25%)	6.8	3,800	7.33	43,300	62
H-18	Untreated Halby Soil/Buffer Solution	None	8,900	9.67	30,800	—
H-19	Treated Halby Soil/Buffer Solution/H_2O_2 (25%)	15.3	1,200	6.71	46,400	86.5
H-20	Untreated Halby Soil/Buffer Solution	None	18,000	9.40	34,900	—
H-21	Treated Halby Soil/Buffer Solution/Perborate	15.1	170	10.47	29,900	99.1
H-22	Untreated Halby Soil/Caustic	None	28,000	8.18	72,000	—
H-23	Treated Halby Soil/Caustic/H_2O_2 (25%)	2.4	7,000	7.66	56,200	75

Table 5 ***Performance Data from Treatment of Halby Site Soils (continued)***

Sample ID	Sample Make-up	Oxidant/CS_2 Molar Ratio	CS_2 (ppm)	pH	COD (ppm)	%CS_2 Reduction
H-24	Untreated Halby Soil/Caustic	None	19,000	8.89	46,600	—
H-25	Treated Halby Soil/Caustic/H_2O_2 (25%)	7.1	2,200	8.04	48,900	88.4
H-25A	Treated Halby Soil/Caustic/H_2O_2 (25%) - Sequential Addition (72 hr. delay)	7.1	2,400	6.86	46,500	87.4

Table 6 Calculations for Percent Reduction in CS_2 Concentrations

Oxidant	Experiment Number	Actual Stoichiometric Ratio[a]	Actual Molar Ratio	% CS_2 Reduction
Percarbonate	H-6			
	H-7	$0.25 \times \frac{34,000}{17,000} = 0.50$	4.0	70
	H-8			
	H-9	$0.5 \times \frac{34,000}{17,000} = 1.0$	8.0	97
	H-10			
	H-11	$1.0 \times \frac{34,000}{16,000} = 2.12$	17.0	99.9+
Perborate	H-12			
	H-13	$0.25 \times \frac{34,000}{23,000} = 0.36$	2.9	71
	H-14			
	H-15	$0.5 \times \frac{34,000}{12,000} = 1.41$	11.3	96
	H-20			
	H-21	$1.0 \times \frac{34,000}{18,000} = 1.88$	15.1	99.1
H_2O_2	H-16			
	H-17	$0.25 \times \frac{34,000}{10,000} = 0.85$	6.8	62
	H-18		15.3	86.52
	H-19	$0.5 \times \frac{34,000}{8,900} = 1.91$		
	H-22			
	H-23	$0.25 \times \frac{34,000}{28,000} = 0.3$	2.4	75
	H-24			
	H-25, H-25A	$0.5 \times \frac{34,000}{19,000} = 0.89$	7.1	88.4, 87.4

(a) $\text{assumed stoichiometric ratio} \times \frac{\text{expected } CS_2 \text{ conc. in soil}}{\text{actual } CS_2 \text{ conc. in soil}} = \text{actual stoichiometric ratio}$

Table 7 *Thiocyanate and Sulfur Levels in Treated and Untreated Halby Soils*

Sample ID	Sample Make-up	Thiocyanate Concentration (mg/kg)	Elemental Sulfur Concentration (%)
H-16	Untreated Halby Soil/Buffer Solution	—	3.45
H-17	Treated Halby Soil/Buffer Solution/H_2O_2 (25%)	—	4.14
H-18	Untreated Halby Soil/Buffer Solution	—	4.71
H-19	Treated Halby Soil/Buffer Solution/H_2O_2 (25%)	—	3.69
H-22	Untreated Halby Soil/Caustic	13,700	4.10
H-23	Treated Halby Soil/Caustic/H_2O_2 (25%)	10,400	5.61
H-24	Untreated Halby Soil/Caustic	8,010	6.73
H-25	Treated Halby Soil/Caustic/H_2O_2 (25%)	7,360	3.86
H-25A	Treated Halby Soil/Caustic/H_2O_2 (25%) — Sequential Addition (72 hr. delay)	4,300	—

Table 8 ***Metals Content and Leachability of Halby Site Soils***

Sample ID	Sample Make-up	pH	Total Metal Concentration, mg/kg				Leachable Metal Concentration, mg/l**			
			Arsenic	Beryllium	Copper	Manganese	Arsenic	Beryllium	Copper	Manganese
H-8	Untreated Halby Soil/Buffer Solution	8.90	799	0.54B	3,490	227*	2.6	<0.001	<0.013	1.6
H-9	Treated Halby Soil/Buffer Solution/Percarbonate	10.06	738	0.56B	2,520	219*	0.33	<0.001	0.97	2.0
H-10	Untreated Halby Soil/Buffer Solution	8.86	749	0.63B	2,090	232*	4.4	<0.001	<0.013	1.8
H-11	Treated Halby Soil/Buffer Solution/Percarbonate	10.26	530	0.46B	1,750	170*	0.21	<0.001	0.96	1.4
H-16	Untreated Halby Soil/Buffer Solution	9.58	972	0.64B	6,660	504*	0.58	<0.001	<0.013	4.9
H-17	Treated Halby Soil/Buffer Solution/H_2O_2 (25%)	7.33	1,090	0.50B	5,600	535*	0.08	<0.001	<0.013	6.8
H-18	Untreated Halby Soil/Buffer Solution	9.67	1,080	0.48B	5,010	498*	1.00	<0.001	<0.013	5.6
H-19	Treated Halby Soil/Buffer Solution/H_2O_2 (25%)	6.71	1,120	0.88B	5,310	996*	0.09	<0.001	12.6	10.6

B-result estimated; level between contract required detection limit and instrument detection limit

*-duplicate analysis outside acceptable quality control limits

**-all leachable metals data are preliminary and should be considered as estimated values pending final confirmation by the laboratory.

NOTE: Data not subjected to ERM comprehensive quality assurance review. The results reported are as received from the laboratory.

Appendix A
References on the Treatability of Carbon Disulfide and Related Compounds

APPENDIX A
REFERENCES ON THE TREATABILITY OF
CARBON DISULFIDE AND RELATED COMPOUNDS

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Appendix B
Treatability Study Analytical Data Backup

APPENDIX B
ANALYTICAL DATA PACKAGES

The following samples are included in the data packages contained in this appendix:

- Raw Halby soil, three samples, as collected from the site: CS_2
- Raw Halby soil data, after receipt at the treatability laboratory: CS_2
- Large-scale samples H-6 through H-9: COD and pH
- Large-scale samples H-10 through H-13: COD and pH
- Large-scale samples H-14 through H-17: COD and pH
- Large-scale samples H-18 through H-21: COD and pH
- Large-scale samples H-6 through H-21: CS_2
- Large-scale samples H-8, 9, 10, 11, 16, 17, 18, and 19: Total arsenic, beryllium, copper, and manganese; preliminary screening data (**not finalized by the laboratory**) for TCLP leachable arsenic, beryllium, copper, and manganese (note that no data package is available at this time for these data)
- Large-scale samples H-16 through H-19 and Supplemental Samples H-22 through H-25: Elemental Sulfur (note that no data package is available at this time for these data)
- Supplemental samples H-22 through H-24, H-25A: CS_2 (note that no data package is available at this time for these data)
- Supplemental sample H-25: Volatile organics (including CS_2) plus TICs (note that no data package is available at this time for these data)
- Supplemental samples H-22 through H-25, H-25A: COD, thiocyanate, and pH (note that no data package is available at this time for these data)

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(Red)

Appendix C
HPLC Screening Method for Carbon Disulfide

Carbon Disulfide Sample Analysis

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CARBON DISULFIDE SAMPLE ANALYSIS

A.1 *INTRODUCTION*

An open loop isocratic HPLC analytical system was used to screen soil samples and determine the amount of CS_2 in spiked, treated, and untreated small-scale soil samples.

A.2 *HPLC SYSTEM*

A.2.1 *CONFIGURATION*

The HPLC system is composed of the following components:

Spectraphysics 8815 Isocratic High Pressure Pump

Rhedyne 7125 Injector Valve with 10 µl loop

Timberline Column Oven at 30.0°C

Jones 25 cm x 4.6 cm C18 (5 µm) separation column

Linear Model 200 UV/VIS Detector

Spectraphysics SP4400 Integrator

Thermo Separation Products Winner on Windows Data Software Package

Computer (386SX 25 Mhz CPU) System using Windows 3.1, WordPerfect for Window 5.1, Excel 4.0 for Windows and Quick Basic

Acrodisc CR PTFE (0.2 µm) Syringe Filter

Cole-Parmer Model 8891 Ultrasonic Mixer

Ohaus Analytical Plus Balance

Laboratory Glassware, Reagents and Supplies

- 100.0 ml volumetric flasks (Class A)
- Volumetric pipets (Class A)
- Pipet bulbs
- 100 µl gas tight Hamilton Syringe
- HPLC grade acetone (Baker Analyzed Solvent)

- HPLC grade methanol (Baker Analyzed Solvent)
- HPLC grade water (Baker Analyzed Solvent)

A.2.2 STANDARDS AND SAMPLE PREPARATION

The CS_2 standards were prepared by diluting a known amount of reagent-grade CS_2 with HPLC-grade methanol in a 100-ml volumetric flask. A 50-ml volumetric pipet was then used to transfer an aliquot from the first flask to another 100-ml volumetric flask, which was filled to volume with HPLC-grade methanol. This method was repeated twice more and used to generate a four-point curve from 1,000 ppm to 625 ppm.

Soil samples were processed for analysis using the following procedure.

1. Tare a 40 ml VOA vial on analytical scale.
2. Weigh out sample placed directly in the VOA vial.
3. Add 1 N HCl to yield a pH <2 (approx. 1 g).
4. Weigh sample on analytical scale (to determine the quantity of acid added) and recrod weight in logbook.
5. Dilute sample to volume with HPLC-grade methanol (with no head space). Record weight of result.
6. Let stand for 24 hours.
7. Draw approximately 3 mls of sample into syringe.
8. Remove needle and attach filter (Acrodic CR PTFE (0.2 μm)).
9. Filter sample into small vial and mark vial with sample number.

A.2.3 MOBILE PHASE PREPARATION

The HPLC mobile phase was prepared to produce a solution of 82% volume methanol and 18% of water. The solution was prepared by mixing 2,000 ml of HPLC-grade methanol with 439 ml of HPLC-grade water.

1. Depending on the amount of mobile phase being mixed, measure out 220 ml of HPLC H_2O for every 1,000 ml of HPLC methanol.
2. Degas new mobile phase with helium for 5 minutes and keep a slight overpressure of helium during HPLC operation.

A.3.0 HPLC CALIBRATION AND ANALYSIS PROCEDURE

A.3.1 CALIBRATION CURVE

Four calibration points were used. Each point was injected two times. Before each analysis, a sample of methanol spiked with a known amount of CS_2 was injected on the HPLC to check the accuracy of the instrument. Spike recovery was consistently greater than 70%, which was deemed adequate for screening purposes.

A.3.2 HPLC ANALYSIS PROCEDURE

Liquid Chromatographic Parameters

Column	Jones 25 cm x 4.6 C18 (5 µm particle size)
Mobile Phase	82% Methanol - 18% Water
Flow Rate	1.0 mls/min
Detector Sensitivity	0.1 AUFS
Volume Injected	60 µl
Wavelength	315 nm

Analytical Procedure

The standard solutions were injected a sufficient number of times to ensure reproducibility. Then each sample was injected. The concentration of the analytes in the sample was calculated by comparing the peak area of the sample to that of the standards. Thermo Separation Products' Winner on Windows software was used to electronically reduce the raw integration data.

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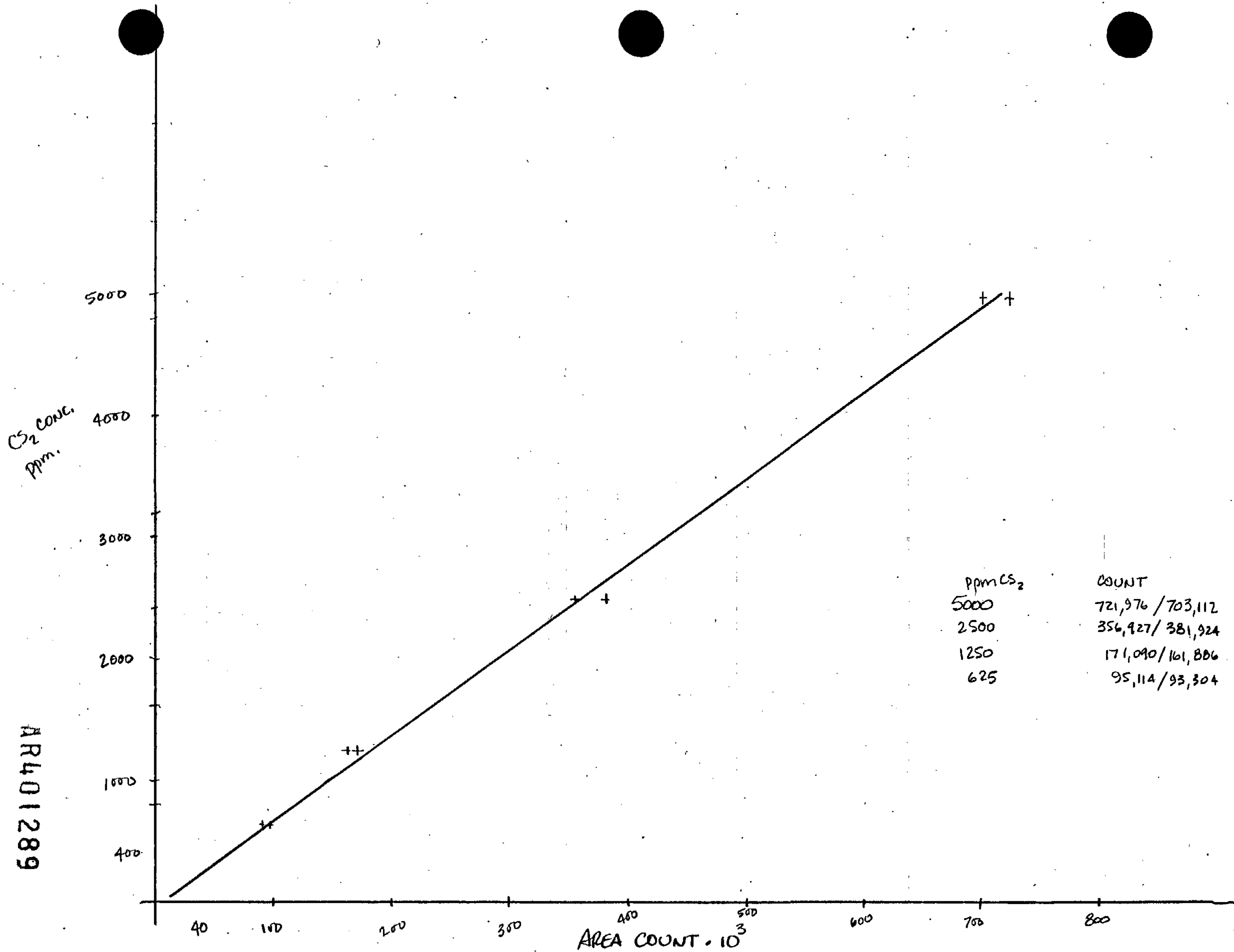
HPLC Calibration Data


CS_2 CONC. ppm.
5000
4000
3000
2000
1000
400
40
100
200
300
400
500
600
700
800
AREA COUNT · 10^3
ppm CS_2
5000
2500
1250
625
COUNT
721,976 / 703,112
356,927 / 381,924
171,090 / 161,886
95,114 / 93,304

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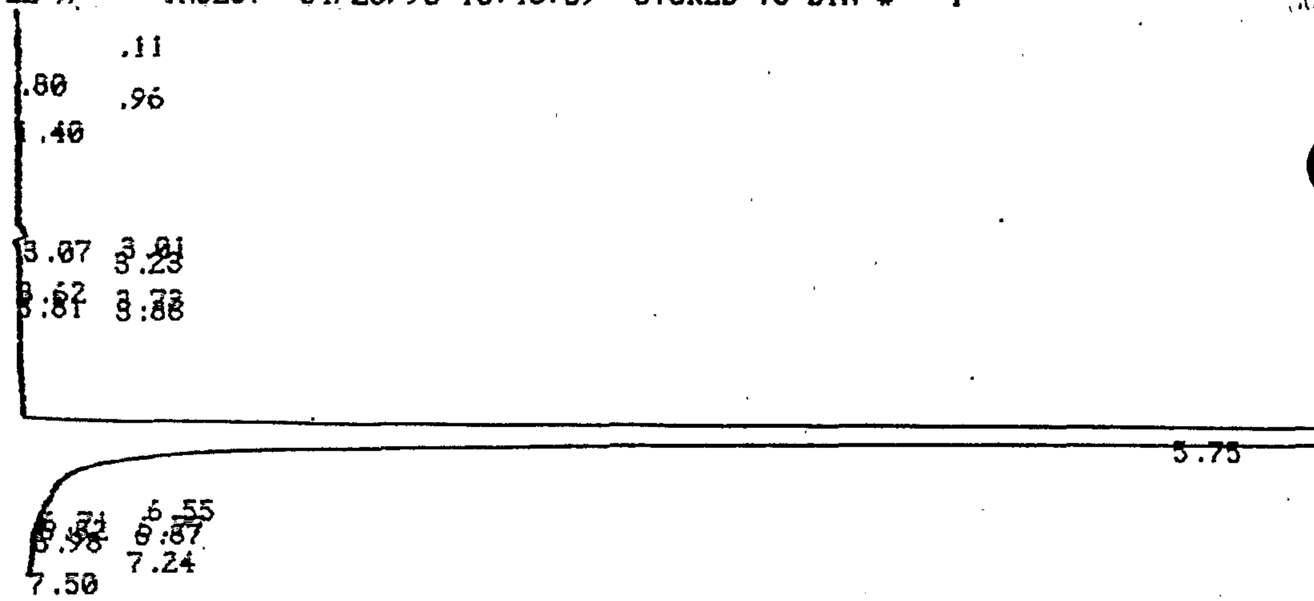
CHANNEL A INJECT 04/28/96 13:48:59 STORED TO BIN # 1



DATA SAVED TO BIN # 1

04/28/96 13:48:59 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 1 INDEX 1 BIN 1

PEAK#	AREA%	RT	AREA	BC
1	0.026	0.11	188	01
2	0.018	0.8	130	02
3	0.042	0.96	306	02
4	0.024	1.4	172	03
5	0.074	3.01	537	02
6	0.059	3.07	429	02
7	0.126	3.23	915	02
8	0.021	3.62	155	02
9	0.016	3.73	113	02
10	0.006	3.81	45	02
11	0.012	3.86	88	03
12	99.496	5.75	721976	08
13	0.005	6.55	37	05
14	0.001	6.71	5	05
15	0.003	6.77	25	05
16	0.003	6.82	22	06
17	0.006	6.87	46	06
18	0.006	6.98	45	06
19	0.04	7.24	291	06
20	0.015	7.5	109	07
TOTAL	100.		725634	

CS_2 Standard
5000 ppm

TD=
FI= 1. FE= 1. MN= 0.
PRESS 'ENTER' TO SKIP ENTRY
ENABLE BASELINE DRAWING? [Y/N] (N) Y
STORAGE MENU? [Y,N] (N)Y

188

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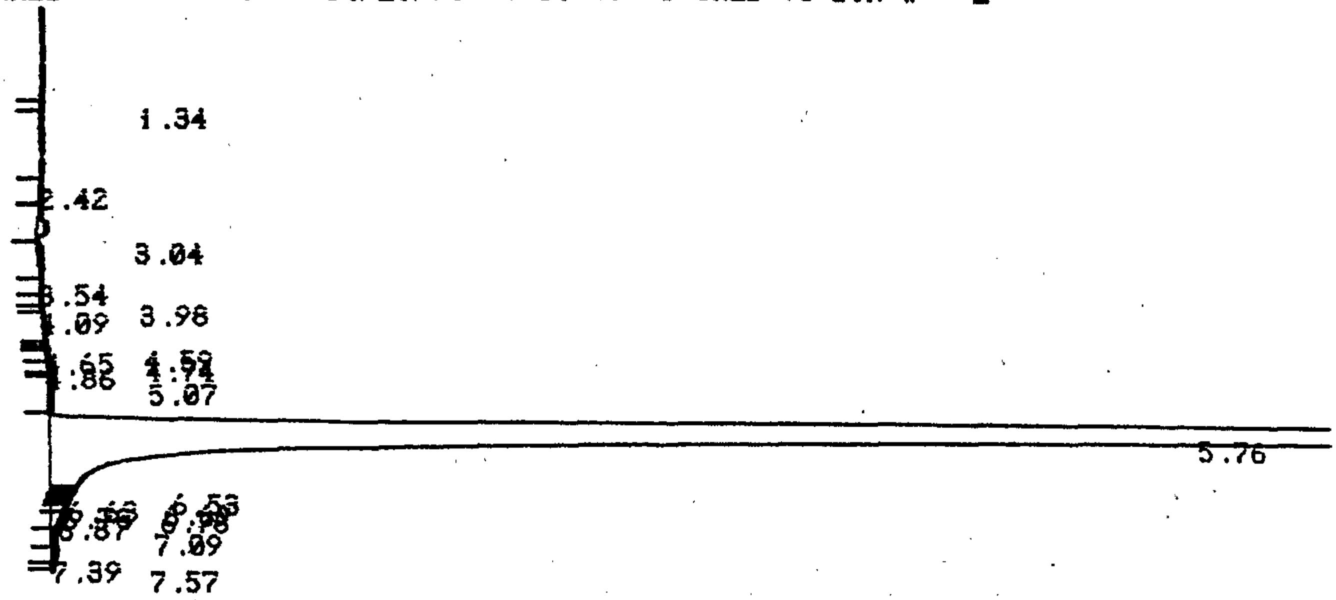
(Red)

CHANNEL A INJECT 04/28/96 14:04:41 STORED TO BIN # 2



DATA SAVED TO BIN # 2

CS2 04/28/96 14:04:41 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 2 INDEX 2 BIN 2

PEAK#	AREA%	RT	AREA BC
1	0.004	1.34	27 01
2	0.17	3.04	1200 02
3	0.095	3.54	669 03
4	0.011	3.98	81 02
5	0.005	4.09	38 03
6	0.004	4.59	29 02
7	0.008	4.65	56 02
8	0.02	4.74	143 02
9	0.011	4.86	76 03
10	0.058	5.07	410 02
11	99.574	5.76	703112 08
12	0.003	6.53	18 05
13	0.003	6.63	21 05
14	0.	6.73	3 06
15	0.	6.87	1 06
16	0.006	7.09	41 06
17	0.026	7.39	185 06
18	0.001	7.57	8 07
TOTAL	100.		706118

CS_2 Standard
5000 ppm

CHANNEL A INJECT 04/28/96 14:14:28 STORED TO BIN # 3

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CHANNEL A INJECT 04/28/96 14:14:28 STORED TO BIN # 3

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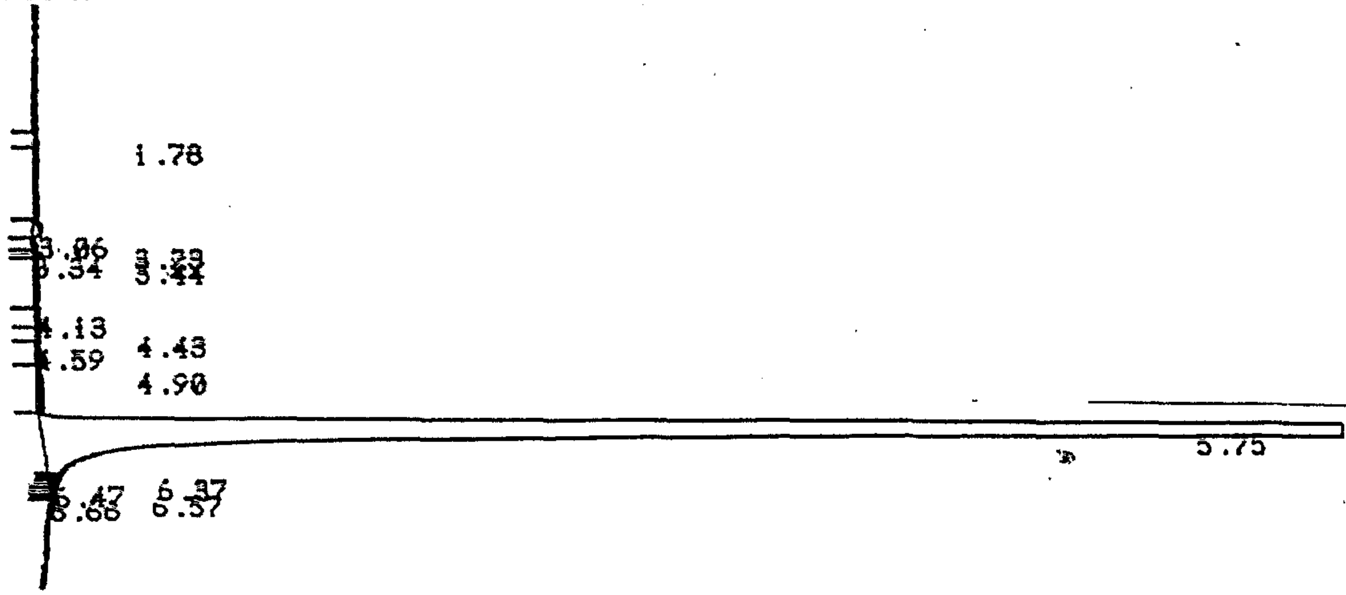

DATA SAVED TO BIN # 3

CS2 04/28/96 14:14:28 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 3 INDEX 3 BIN 3

PEAK#	AREA%	RT	AREA	BC
1	0.02	1.78	71	01
2	0.263	3.06	954	02
3	0.09	3.23	325	02
4	0.083	3.34	302	02
5	0.409	3.44	1485	02
6	0.141	4.13	512	02
7	0.083	4.43	302	02
8	0.125	4.59	453	02
9	0.347	4.9	1257	02
10	98.422	5.75	356927	08
11	0.001	6.37	4	05
12	0.001	6.47	4	05
13	0.015	6.57	54	07
TOTAL	100.		362650	

CS_2 Standard
2500 ppm

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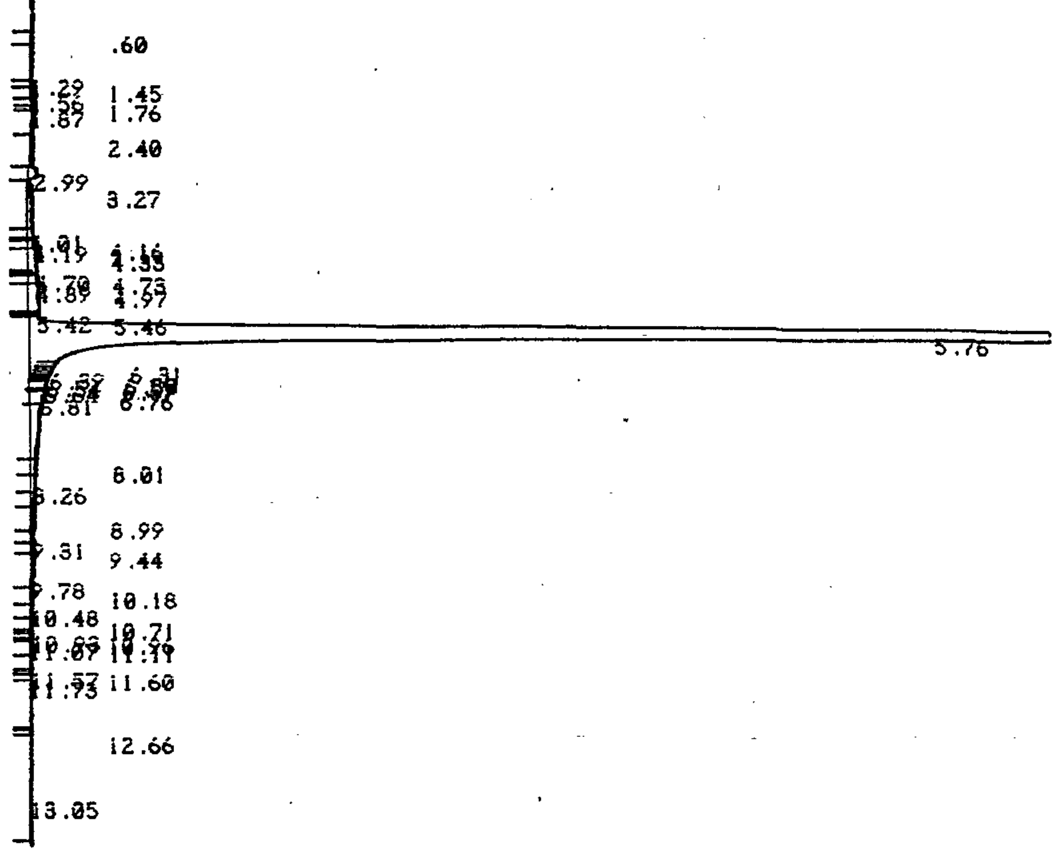
CHANNEL A INJECT 04/28/96 14:35:48 STORED TO BIN # 4

191



DATA SAVED TO BIN # 4

CS2 04/28/96 14:35:48 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 4 INDEX 4 BIN 4

PEAK#	AREA%	RT	AREA	BC
1	0.046	0.6	193	02
2	0.172	1.29	693	02
3	0.03	1.45	121	02
4	0.052	1.56	210	02
5	0.031	1.76	124	02
6	0.009	1.87	38	03
7	0.246	2.4	992	02
8	0.326	2.99	1315	02
9	0.711	3.27	2868	02
10	0.165	4.01	665	02
11	0.05	4.16	203	02
12	0.189	4.19	763	02
13	0.609	4.33	2455	02
14	0.075	4.7	302	02
15	0.077	4.73	311	02
16	0.294	4.89	1186	02
17	1.073	4.97	4327	02
18	0.097	5.42	392	02
19	0.088	5.46	354	02
20	94.682	5.76	381924	09
21	0.005	6.39	19	05
22	0.006	6.5	24	06
23	0.002	6.54	10	06
24	0.01	6.57	39	06
25	0.005	6.64	20	07
26	0.043	8.01	172	06
27	0.021	8.26	84	07
28	0.103	8.99	416	06
29	0.074	9.31	297	06
30	0.055	9.44	220	06

CS_2 Standard
2500 ppm

192

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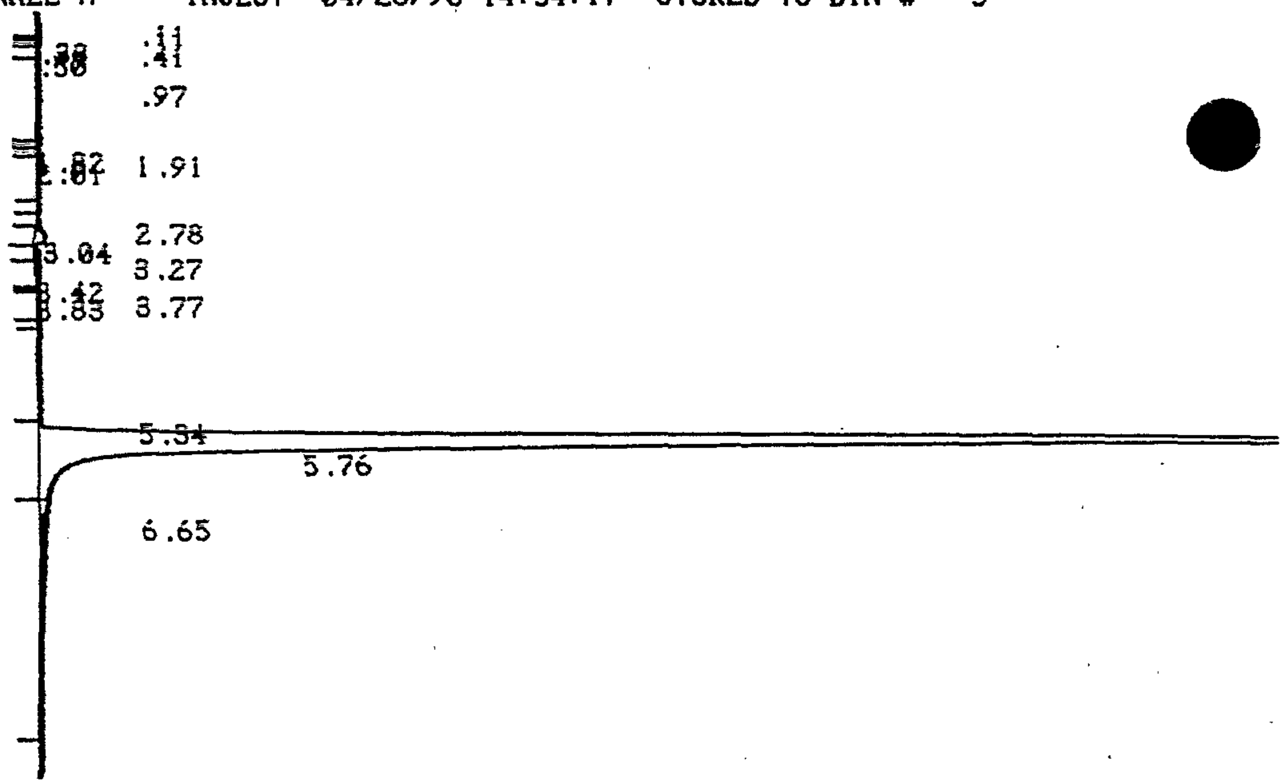
CHANNEL A INJECT 04/28/96 14:54:17 STORED TO BIN # 5



DATA SAVED TO BIN # 5

CS2 04/28/96 14:54:17 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 5 INDEX 5 BIN 5

PEAK#	AREA%	RT	AREA	BC
1	0.145	0.11	265	02
2	0.021	0.38	39	02
3	0.043	0.41	79	02
4	0.12	0.5	219	02
5	0.606	0.97	1109	02
6	0.057	1.82	104	02
7	0.07	1.91	129	02
8	0.049	2.01	90	03
9	0.097	2.78	178	02
10	0.704	3.04	1288	02
11	0.326	3.27	597	02
12	0.492	3.42	900	02
13	0.056	3.77	102	02
14	0.243	3.83	445	03
15	0.58	5.34	1062	02
16	93.491	5.76	171090	02
17	2.899	6.65	5305	03
TOTAL	100.		183001	

CS_2 Standard
1250 ppm

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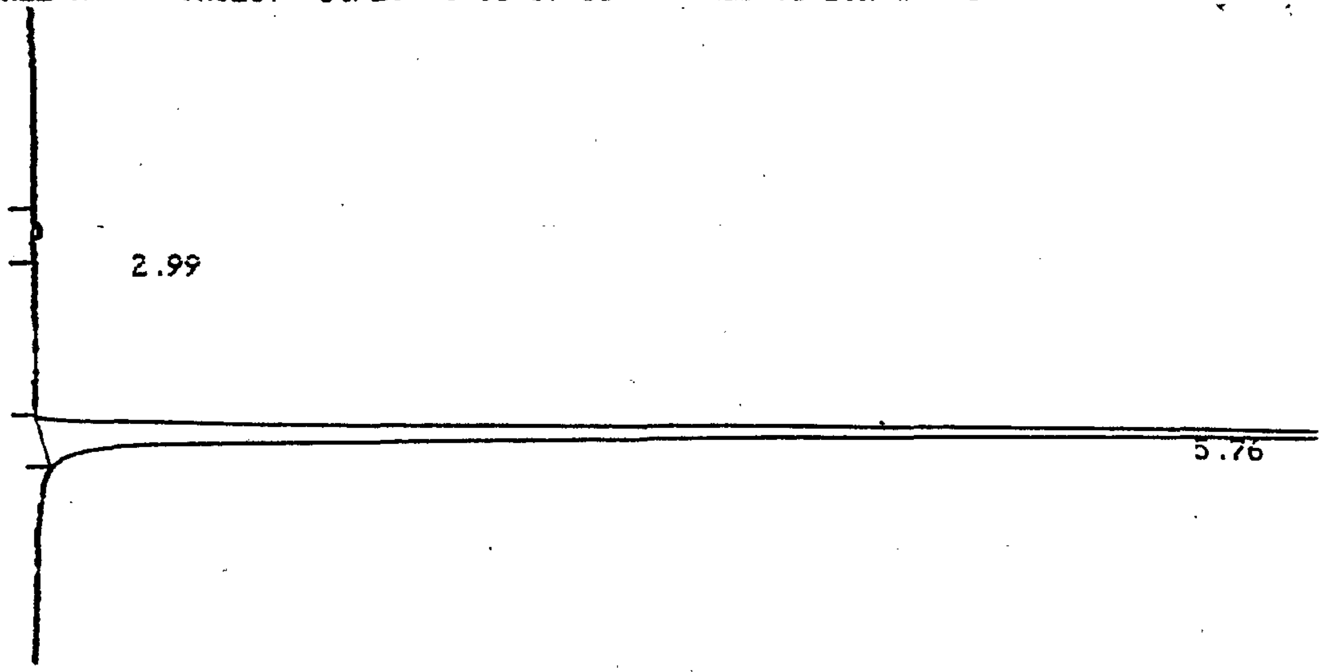
PT EVAL:

CHANNEL A   INJECT 04/28/96 15:07:30   STORED TO BIN #   6



DATA SAVED TO BIN #   6

CS2   04/28/96 15:07:30   CH= "A"   PS= 1.

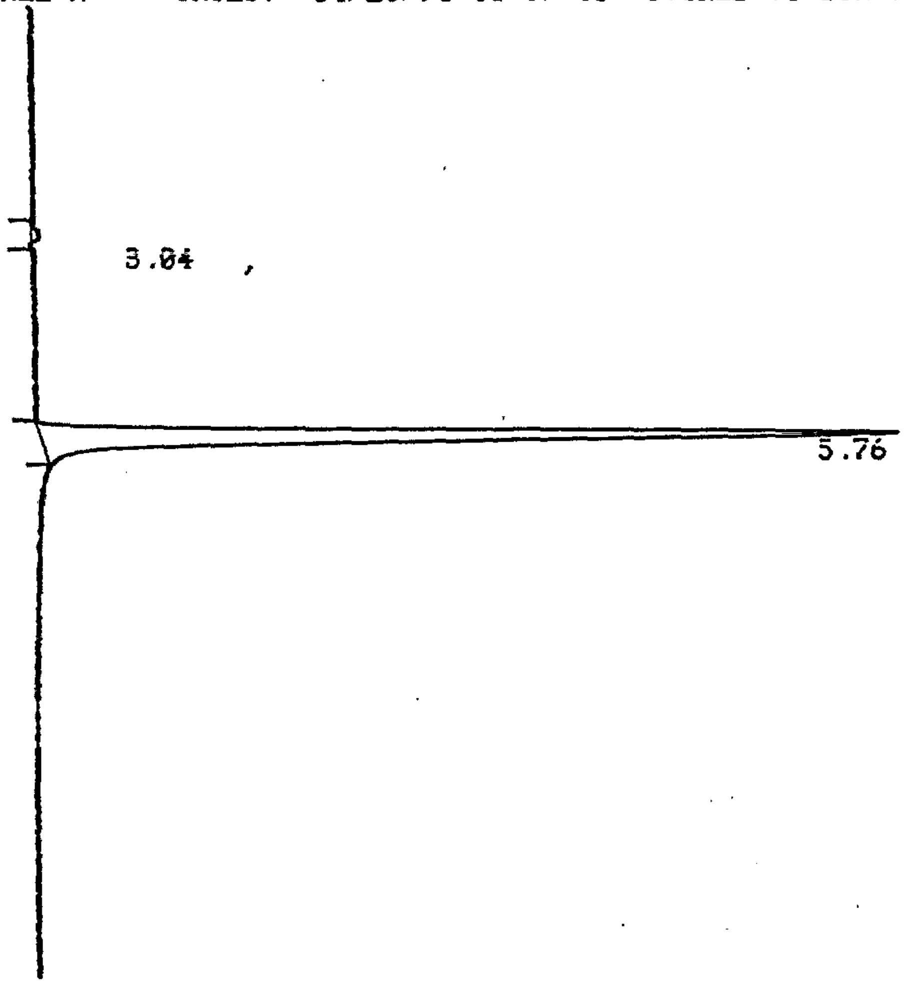
FILE 1.   METHOD 0.   RUN   6   INDEX   6   BIN   6

PEAK#	AREA%	RT	AREA BC
1	0.228	2.99	370 01
2	99.772	5.76	161886 01
TOTAL	100.		162256

CS_2 Standard
1250 ppm

TOTAL 100. 162256

CHANNEL A INJECT 04/28/96 15:19:46 STORED TO BIN # 7



DATA SAVED TO BIN # 7

CS2 04/28/96 15:19:46 CH= "A" PS= 1.

FILE 1. METHOD 0. RUN 7 INDEX 7 BIN 7

PEAK#	AREA%	RT	AREA	BC
1	0.541	3.04	517	01
2	99.459	5.76	95114	01
TOTAL	100.		95631	

CS_2 Standard
625 ppm

CHANNEL A INJECT 04/28/96 15:38:11 STORED TO BIN # 8

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